A Laboratory Performance Check for the Determination of Metals (Hg, Zn, Cd, Cu, Pb) in Reference Marine Sediments

R.W. Macdonald[1] and H. Nelson[2]

[1]Institute of Ocean Sciences
Department of Fisheries and Oceans
Sidney, B.C., V8L 4B2

[2]Environmental Protection Service
Environment Canada
Kapilano 100, Park Royal
West Vancouver, B.C., V7T 1A2

1984

Canadian Technical Report of Hydrography and Ocean Sciences No. 33

Canadian Technical Report of Hydrography and Ocean Sciences

These reports contain scientific and technical information of a type that represents a contribution to existing knowledge but which is not normally found in the primary literature. The subject matter is generally related to programs and interests of the Ocean Science and Surveys (OSS) sector of the Department of Fisheries and Oceans.

Technical Reports may be cited as full publications. The correct citation appears above the abstract of each report. Each report will be abstracted in Aquatic Sciences and Fisheries Abstracts. Reports are also listed in the Department's annual index to scientific and technical publications.

Technical Reports are produced regionally but are numbered and indexed nationally. Requests for individual reports will be fulfilled by the issuing establishment listed on the front cover and title page. Out of stock reports will be supplied for a fee by commercial agents.

Regional and headquarters establishments of Ocean Science and Surveys ceased publication of their various report series as of December 1981. A complete listing of these publications and the last number issued under each title are published in the *Canadian Journal of Fisheries and Aquatic Sciences*, Volume 38: Index to Publications 1981. The current series began with Report Number 1 in January 1982.

Rapport technique canadien sur l'hydrographie et les sciences océaniques

Ces rapports contiennent des renseignements scientifiques et techniques qui constituent une contribution aux connaissances actuelles mais que l'on ne trouve pas normalement dans les revues scientifiques. Le sujet est généralement rattaché aux programmes et intérêts du service des Sciences et Levés océaniques (SLO) du ministère des Pêches et des Océans.

Les rapports techniques peuvent être considérés comme des publications à part entière. Le titre exact figure au-dessus du résumé du chaque rapport. Les résumés des rapports seront publiés dans la revue Résumés des sciences aquatiques et halieutiques et les titres figureront dans l'index annuel des publications scientifiques et techniques du Ministère.

Les rapports techniques sont produits à l'échelon régional mais sont numérotés et placés dans l'index à l'échelon national. Les demandes de rapports seront satisfaites par l'établissement auteur dont le nom figure sur la couverture et la page de titre. Les rapports épuisés seront fournis contre rétribution par des agents commerciaux.

Les établissements des Sciences et Levés océaniques dans les régions et à l'administration centrale ont cessé de publier leurs diverses séries de rapports depuis décembre 1981. Vous trouverez dans l'index des publications du volume 38 du *Journal canadien des sciences halieutiques et aquatiques*, la liste de ces publications ainsi que le dernier numéro paru dans chaque catégorie. La nouvelle série a commencé avec la publication du Rapport n° 1 en janvier 1982.

Canadian Technical Report of Hydrography and Ocean Sciences No. 33

1984

A Laboratory Performance Check for the Determination of Metals (Hg, Zn, Cd, Cu, Pb) in Reference Marine Sediments

by

R.W. Macdonald [1] and H. Nelson [2]

1. Institute of Ocean Sciences
Department of Fisheries and Oceans
Sidney, B.C. V8L 4B2

and

2. Environmental Protection Service
Environment Canada
Kapilano 100, Park Royal
West Vancouver, B.C. V7T 1A2

Institute of Ocean Sciences
Department of Fisheries and Oceans
Sidney, B.C. V8L 4B2

Copyright Minister of Supply and Services Canada - 1984

Cat. No. Fs 97-18/ 33 ISSN 0711-6764

Correct citation for this report is:

Macdonald, R.W. and H. Nelson. 1984. A Laboratory Performance Check for the Determination of Metals (Hg, Zn, Cd, Cu, Pb) in Reference Marine Sediments. Can. Technical Rep. Hydrogr. Ocean Sci : No. 33: 57 pp

CONTENTS

	Page
Acknowledgements	iv
Abstract/Résumé	v
1. INTRODUCTION	1
2. EXPERIMENTAL DESIGN	4
2.1 PREPARATION OF SECONDARY REFERENCE MARINE SEDIMENT	5
2.2 INSTRUCTIONS TO LABORATORIES	6
2.3 STATISTICAL TREATMENT OF THE DATA	6
3. RESULTS	7
4. EVALUATION OF LABORATORY PERFORMANCE	8
4.1 SAMPLE TREATMENT : RE-HYDRATED VERSUS DRY REFERENCE MATERIAL	8
4.2 RANKING OF LABORATORIES	8
4.3 GRAPHICAL DIAGNOSIS	14
5. CONCLUSIONS	19
REFERENCES	24
APPENDIX 1 : DATA SUMMARIES	27
LAB 1	29
LAB 2	33
LAB 3	37
LAB 4	41
LAB 5	45
LAB 6	49
LAB 7	53
APPENDIX 2 : MARINE SEDIMENT REFERENCE MATERIALS MESS-1, BCSS-1	55

ACKNOWLEDGEMENTS

Many reviewed earlier drafts of this report and provided useful comment which has been incorporated into this final version. In particular we thank Drs.D. MacGregor and P. Cohen for thoroughly checking and rechecking the text and suggesting numerous clarifications and improvements. We thank Dr. S. Berman for his kind comments and for taking us to task on a number of points. Others who provided comment and stimulating discussion include A. Cornford, P. Erickson, D. Morse, H. Samant, V.J. Stukas, D.J. Thomas, J.A.J. Thompson, M. Waldichuk, M. Yunker and V. Zitko. While indebted to the reviewers, we must take full responsibility for any errors or omissions which occur. S. Thomson lent editorial assistance, C. Priestley typed the manuscript, and I. Szabo prepared the drawings. Lastly, we acknowledge and thank the seven laboratories that participated (albeit involuntarily) in this study.

ABSTRACT

Macdonald R.W. and H. Nelson, 1984. A Laboratory Performance Check for the Determination of Metals (Hg, Zn, Cd, Cu, Pb) in Reference Marine Sediments. Can. Tech. Rep. Hydrogr. Ocean Sci. 33: 57 pp

A laboratory performance check for metal determinations in marine sediments was carried out for seven laboratories from the Canadian Pacific Region. Each laboratory was given three reference sediments in replicate (n = 4) to analyze for Hg, Zn, Cd, Cu and Pb. Samples were disguised and the laboratories were not informed of the true identity or of our reasons for having analyses performed. For Hg, two laboratories could perform accurate measurements on the reference materials (BCSS-1, MESS-1). Two other laboratories had good precision but were subject to bias and the remaining laboratories provided data which were less accurate and precise. The data were at most a factor of three away from the reliable value for the reference sediments. For Cd, three laboratories had accurate determinations at the Ocean Dumping limit of 0.6 $\mu g\ g^{-1}$ (dry weight), and two of these laboratories accurately determined Cd at the 0.25 $\mu g\ g^{-1}$ concentration. Another two laboratories could discriminate between the two references, but had bias in their results. Two laboratories could not perform Cd determinations at the Ocean Dumping limit. The performance for the above two metals as well as Zn, Cu and Pb is detailed in the report. Major difficulties in interpreting data from the seven laboratories included the lack of information about procedures, instrumentation, calibration, recovery and interferences, blanks, detection limits, precision and accuracy. Improvement in application of quality assurance procedures and their reporting is essential if reliable data (which can independently be evaluated as such) are to be provided.

Key words: Interlab-comparison, performance check, sediments, Hg, Zn, Cd, Cu, Pb.

RÉSUMÉ

Macdonald R.W. and H. Nelson, 1984. Vérification en laboratoire de l'efficacité des méthodes de dosage des métaux (Hg, Zn, Cd, Cu, Pb) dans des sédiments marins utilisés comme référence - Rep. Hydr. Ocean. Sci. # 33: 57 pp

On a effectué une vérification de l'efficacité des méthodes de dosage des métaux contenus dans des sédiments marins, dans sept laboratoires de la région pacifique du Canada. On a donné à chaque laboratoire trois échantillons, en double, de sédiments de référence (n 4), dont doit être dosé le contenu en Hg, Zn, Cd, Cu et Pb. On a "déguisé" les échantillons, et évité d'informer les laboratoires en question de l'identité véritable des échantillons ou de l'intention véritable de ces analyses. Dans le cas du Hg, deux laboratoires ont pu réaliser des analyses exactes sur les matériaux de référence (BCSS-1, MESS-1). Deux autres laboratoires ont atteint un bon degré de précision, mais des distorsions sont quand même apparues; quant aux autres laboratoires, ils ont fourni des données moins exactes et précises. Au plus, les données se différenciaient d'un facteur de trois de la valeur fiable attribuée aux sédiments de référence. Dans le cas du Cd, trois laboratoires avaient effectué des dosages précis à la limite acceptable de reject en mer de 0,6 µg g^{-1} (poids sec), et deux de ces laboratoires ont dosé avec précision le Cd à la concentration de 0,25 µg g^{-1}. Deux autres laboratoires ont pu établir une distinction entre les deux points de référence, mais leurs résultats étaient biaisés. Deux laboratoires n'ont pu effectuer les dosages du Cd à la limite acceptable susmentionnée. Dans le cas des deux métaux en question (Hg, Cd), et des autres (Zn, Cu et Pb), l'efficacité du dosage est décrite en détail dans le rapport. Parmi les principales difficultés qu'ont rencontrées les sept laboratoires dans l'interprétation des données, figuraient le manque d'information sur les procédés, sur l'appareillage, l'étalonnage, l'acquisition des données, les interférences, les lacunes, les limites de détection, et la précision et l'exactitude des résultats. Il est essentiel d'améliorer l'application des procédés garantissant la qualité et de les noter, si l'on veut fournir des données fiables (qui peuvent être évaluées de façon indépendante comme telles).

Mots-clés: comparaison des résultats entre les laboratoires, vérification de l'efficacité (des méthodes), sédiments, Hg, Zn, Cd, Cu, Pb.

1. INTRODUCTION

The Ocean Dumping Control Act (Canada) concerns itself with prohibited substances including Hg and Cd (Schedule 1), and restricted substances including Zn, Cu and Pb (Schedule 2). To make decisions under these regulations requires data that are accurate within known limits of confidence. It has long been recognized that fulfilling this requirement for environmental samples is difficult, even with well defined analytical methods applied to homogeneous materials. Here we consider the trace elements Hg, Zn, Cd, Cu and Pb in marine sediments. Our problem in reviewing ocean dumping permit applications has been to decide on the acceptability of dredged sediments for marine disposal based on "total" metal determinations by different laboratories applying different methods to a very heterogeneous substrate.

In recognition of the problem, the Atlantic Region of Environment Canada has had an ongoing intercalibration program for several years. (Samant et al, 1979, 1981.) We, in the Pacific Region, have lagged behind, and this intercalibration was designed to rectify the situation. We have titled this exercise a "Laboratory Performance Check" in accordance with the AOAC-CIPAC definition (AOAC, 1974);

> "The analysis of very carefully prepared and homogeneous samples, normally of known active ingredient content, to establish or verify the performance of a laboratory or analyst".

That laboratories use their own methods is implicit in this definition. Our performance check was purposely designed to be "blind" and laboratories were not informed about the true identity of the materials, nor were they aware of our purpose in requesting the analyses. Seven laboratories were involved. Ideally, one would like to use no less than five materials covering a range of metal concentrations appropriate to the ocean dumping regulations and include no fewer than ten laboratories (Mandel and Lashof, 1968). Constraints of money and laboratories willing to do the work, however, restricted us to the less than ideal situation.

A performance check such as this evaluates a number of factors including the method, the analyst, the working environment, and instrumentation available to the analyst. An alteration in a single item in this list could potentially change the results. The analyst is probably the single most important factor and the loss or gain of an analyst may drastically alter a laboratory's capability to do certain analyses. This inter-laboratory study is therefore a "snap-shot" and may not represent the day-to-day performance of the laboratory. While an auditor who has a chance to view laboratory functioning at the "lab bench" level could determine the likelihood of continuity, that is not possible here, and is strictly in the province of the laboratory manager. Therefore, this intercalibration is not primarily intended to show which laboratories are suitable for carrying out metal analyses on sediments, although it could be used, as is done here, to evaluate the laboratory performance at the time analyses were run. Rather our purposes were:

(1) To establish which methods employed by the 7 laboratories enable satisfactory determination of total metal content of sediments;

(2) To assess the quality assurance process used by laboratories;

(3) To determine omissions and inadequacies in present analytical and reporting practices.

To be truly useful intercalibration should become a continual process with rapid feedback in which the reviewers and laboratories share. Both have much to gain by the regular reporting of reliable data.

In this study we have used NRC reference materials (MESS-1, BCSS-1) plus one of our own making. Abbey (1980) prefers the term "reference material" rather than "standard sample" because "the latter name suggests a greater degree of reliability than can realistically be attributed to the derived compositional values". The two reference materials used here clearly are standards of well controlled composition and careful determination. However, most analysts consider standards (particularly primary standards) as materials which satisfy certain requirements: they are easy to obtain, purify and store, can be easily handled without alteration, can be tested for impurities, are soluble or miscible in an appropriate fluid, react stoichiometrically and essentially instantaneously, and for the purposes of

analysis are homogeneous. Reference sediments are unlike primary standards and intentionally so since their value is in representing a material of complex composition. Therefore there seems to be some value in differentiating "standards" and "reference materials" as Abbey suggests and we will follow that terminology here. Reference materials are easily mis-applied due to their complexity and the natural variability of substances they are supposed to represent. For reference sediments there is a statistical requirement for a minimum representative sample size (Ingamells and Switzer, 1973). For our two certified reference sediments, the representativeness is guaranteed for samples greater than 500 mg (Appendix 2) although they are well mixed with respect to trace metals even at less than 100 mg (Berman, pers. comm.). Natural marine sediments contain a complex mixture of inorganic and organic substances, none of which can be considered to be well controlled. Matching an appropriate reference material to the sediment being analyzed is therefore an important consideration. Ideally the reference should have an identical matrix, and a similar concentration of trace constituent distributed identically within the matrix.

In this report we consider the quality of data in terms of bias, precision and accuracy. Some inconsistency exists, primarily in the definition of accuracy (Kirchmer, 1983). We have used the Water Research Centre approach wherein the error, Δ, of an analytical result is defined as $\Delta = Xi - R$ where R the true value, and Xi a particular result. By this definition bias (the difference between the average of a number of determinations and the "true" value) and precision (the tightness of the data grouping) both contribute to accuracy. Later we summarize accuracy by a modified coefficient of variation which is analogous to that used to express precision. The precision is often represented by such parameters as standard deviation, standard error, confidence interval, or tolerance limit. However, each of these is calculated differently and has a different meaning. For example, tolerance limits are the bounds within which a certain proportion of the measurements is expected to lie. Confidence limits, on the other hand, define an interval within which we expect a single sample or a population parameter such as the mean to lie (Natrella and Eisenhart, 1968). Statements about analytical uncertainty should be well formulated and supported or it will be difficult to say exactly what is meant.

Ku (1968) has summarized many of the statements of precision, bias and uncertainty and recommends how they should be used. Furthermore, if statistical comparisons are to be made, at least 3 pieces of information, $\bar{X}$ (the average), s (the standard deviation) and n (number of replicates) are needed. The reason for this is that how well $\bar{X}$ estimates the population mean, μ, depends on both s and n, and how well s estimates σ depends on n. Data which include only estimates of $\bar{X}$ and s are therefore incomplete (Natrella, 1982).

2. EXPERIMENTAL DESIGN

There are a number of requirements which must be met to test the reliability of routine metal determinations (Hg, Zn, Cd, Cu, Pb) on marine sediments:

(1) A marine sediment should be available with uniform properties and whose elemental composition is reliably determined;

(2) The laboratory should not take any special precautions with the samples above and beyond those normally taken with routine samples (Lindgren & McElrath, 1969). Ideally, the laboratory should not know they are working with reference material; and

(3) Sufficient replication or paired samples should be used to evaluate precision.

To satisfy requirement (1) above, we chose two reference marine sediments prepared by NRC (MESS-1, BCSS-1). Appendix 2 lists the relevant properties. Requirement (2) is more difficult to achieve and we chose several strategies. For every laboratory each sediment was subsampled into four separate Whirlpak bags (replicates) and each bag given a false name which could easily be recognized as an "ocean dumping" location. Three of the four sediment subsamples were re-hydrated with known quantities of Milli-Q water. These were then mixed well by kneading the outside of the bags. Moisture content could be calculated because the sediments were weighed into the Whirlpak bags. One of the sediments was left dry so that we could later evaluate the possibility that the re-hydration process in some way compromised the samples. Care was taken to handle the sediments with acid-cleaned plastic implements only. To make it more difficult to guess the identity of the sediments, we prepared a secondary reference of undetermined composition as described below.

This secondary reference was packaged in the same manner as the reference materials, except that water was added to all four Whirlpak bags. Therefore each laboratory received 12 Whirlpak bags, each identified with a geographic location, two of the bags containing dry powder. Even with the identity of the samples disguised as described, it is quite possible that some of the laboratories recognized a pattern. Indeed one laboratory (number 4) commented after reviewing the first draft of this document that "it was obvious to the analyst that there were three samples replicated four times each". To determine this would still require some analytical capability, and a review of the data from laboratory 4 does not indicate that they guessed our intention or what materials we were using.

The third requirement above was fulfilled by supplying four blind replicates for each material to each laboratory. We consider this minimal and would have preferred seven to ten replicates, or alternatively, the use of several paired samples (Youden & Steiner, 1975).

The preparation of our secondary reference serves two purposes. It helps to obscure the identity of the reference materials, and aids in evaluating the potential of making secondary references for future use. A secondary reference has the clear advantage of allowing a wider range of sediment type and elemental concentration to be used for performance evaluation thus limiting the chances that the laboratory performing the analysis would guess the contents of a bag containing reference marine sediments. The pitfall of course is that one must establish that the secondary reference is well mixed with respect to the elements of interest and that a reasonably accurate determination of concentration can be made. We sought to demonstrate the feasibility of this during this study.

2.1 Preparation of Secondary Reference Marine Sediment

Sediment was collected from Vancouver Harbour and wet-sieved. The less than 62 μm fraction was saved, and filtered onto Whatman filters (541). These were then dried, the sediments removed and pulverized in a large porcelain mortar and mixed by shaking in a large polycarbonate bottle.

During preparation, no special cleanliness procedures were practised. The object of the procedure was not to prepare a representative sample of Vancouver Harbour sediments but rather to prepare a well-mixed, fine-grained reference material. Once the sediments were in the polycarbonate bottle they were mixed for two days by rotating on a vertical wheel, shaken vigorously by hand from time to time and then treated as the other reference material. Only acid cleaned plastic implements were used during the transfer processes.

2.2 Instructions to laboratories

No methods were specified to the laboratories because this was not a method evaluation (collaborative study) but rather an investigation of the present performance of laboratories. Each laboratory was asked to determine the total contents of Hg, Cd, Cu and Pb in each sediment sample. Given that Canadian Ocean Dumping limits are 0.6 $\mu g\ g^{-1}$ for Cd and 0.75 $\mu g\ g^{-1}$ for Hg we asked for as low a detection limit (d.l.) as possible. For Cd we requested a d.l. $\leq$ 0.2 $\mu g\ g^{-1}$ (dry weight). Details on methods, the laboratory's estimate of precision, accuracy and d.l. were sought later if these were incompletely reported with the results. (This does not imply that the final product reported is complete, but rather that it is as complete as possible. The information here far exceeds that which normally accompanies data in the Pacific Region, Environmental Protection Service, ocean dumping permit files.)

2.3 Statistical Treatment of the Data

Many statistical methods (for example two-sample t-tests or parametric analysis of variance) require that the measurements come randomly from normal populations with comparable variances. A quick examination of the data presented here suggests that neither assumption is on very solid ground. Environmental samples in general, and particularly trace component determinations, are seldom normally distributed (Samant et al, 1980; Zitko, 1980 a, b), however, well mixed reference material should yield samples (>500mg) with a normal distribution and constant variance. Our problems, here, therefore, stem from the analytical process, and it is known that even simple analytical operations can generate non-Gaussian data (Harris 1978).

Application of Bartlett's test (Zar, 1974) to the data reported here shows that variances are not homogeneous for any of the metals ($P < 0.001$). Unfortunately, Bartlett's test is badly affected by non-normal distributions, a situation which may apply to some of our data. Logarithmic transformations are often used to stabilize variance, or non-parametric methods are applied. We have chosen to use non-parametric or ranking procedures because of the uncertainties in establishing that our data are log-normally distributed (see Thompson and Howarth, 1980, for example). However, a disadvantage of non-parametric methods is that they are conservative, and may fail to demonstrate a difference which is real (error of the second kind). For convenience we have summarized the data using parametric measures (standard deviation) and to gain power have looked at the effect of adding water to the sediments by parametric methods, with the above cautions. Despite these statistical problems we have a distinct advantage in knowing the "reliable" value for two of the sediments.

3. RESULTS

The data provided by the laboratories are arranged in Appendix 1 as Tables A-1 to A-7. The coding used for the samples is shown at the start of the appendix. In each table is given the sample identity (column 1) and moisture content (column 2) followed by the metal data for BCSS-1, MESS-1 and our own secondary reference material OCSS-1. For each metal, and the three reference materials, four replicate determinations are given along with the average, $\bar{X}$, and the standard deviation, s, multiplied by 3.18 ($t_{0.05(2),\,\nu = 3}$);

$$s = \sqrt{\frac{\Sigma X_i^2 - \frac{(\Sigma X_i)^2}{n}}{n - 1}}$$

where n is the number of replicates, and X_i the i^{th} determination. We have multiplied s by the "t" value to make this parameter comparable to the 95% tolerance limits, tol, given by NRC (see Appendix 2) and included in

the tables in Appendix 1. For our own secondary reference, no "reliable values" are reported. The information on methodology supplied to us by the laboratories is located opposite each table, and below that we provide a concise critique of the data and ancillary information. Data were evaluated in the following nine categories: (1) Laboratory procedures; (2) Instrumentation; (3) Calibration; (4) Recovery checks; (5) Blanks; (6) Detection limits; (7) Precision; (8) Accuracy checks; and (9) Quality control. The critique is provided not so much as a condemnation of the laboratories, for we have all been remiss in reporting data completely; rather we wanted to show the problems of judging the validity of the data given the information provided.

4. EVALUATION OF LABORATORY PERFORMANCE

4.1 Sample Treatment: Re-hydrated Versus Dry Reference Material

As noted in the experimental design, we deliberately left one subsample each of MESS-1 and BCSS-1 in the dry state. Two possibilities come to mind: (1) Adding Milli-Q water in some way alters or contaminates the reference material; and (2) The laboratory might treat the dry and wet samples differently. Both cases can be evaluated by asking if there is a difference between results for dry reference sediment and results for disguised re-hydrated reference sediment. Consequently we have the following null hypothesis;

"H_o: Difference between determinations and the NRC "reliable" value (X_i-R) for a given metal is the same for dry sediment and re-hydrated sediment."

We tested this hypothesis for each metal using the two-tailed Mann-Whitney non-parametric procedure (Zar, 1974) and the more powerful but less conservative Student's 't' test. In each case we chose $\alpha = 0.05$ ($n = 56$, 14 dry, 42 re-hydrated). In no case was the null hypothesis rejected and therefore we consider the reference materials to be unaltered in their metal contents by the process of re-hydration.

4.2 Ranking of Laboratories

Table 1 summarizes our estimates of precision and accuracy for the

Table 1. Summary of Precision and Accuracy as measured by Coefficient of Variation

LAB	MATERIAL	PRECISION (C.V.) [1] Hg	Zn	Cd	Cu	Pb	ACCURACY (MODIFIED C.V.) [2] Hg	Zn	Cd	Cu	Pb
1	BCSS-1	24.5	20.4	4.2	6.8	13.2	72	19	370	35	32
	MESS-1	41.4	3.1	4.3	7.8	7.5	42	15	129	35	8
	OCSS-1	43.6	18.2	21.2	14.1	8.9					
2	BCSS-1	9.5	6.6	14.8	12.1	7.2	24	14	>49	52	13
	MESS-1	9.3	7.8	3.0	2.2	11.2	22	15	4	48	25
	OCSS-1	3.5	5.8	10.8	1.3	7.1					
3	BCSS-1	15.2	1.8	17.4	0.8	4.7	13	15	18	12	28
	MESS-1	7.5	2.5	2.2	2.1	5.0	8	13	7	8	29
	OCSS-1	8.3	0.9	7.8	2.2	8.3					
4	BCSS-1	16.7	3.9	0-14 [3]	5.7	0-29 [3]	56	12	60	10	12
	MESS-1	7.5	3.3	0-58 [3]	6.1	3.5	26	15	32	10	19
	OCSS-1	7.8	2.7	2.3	2.3	3.0					
5	BCSS-1	87.1	16.4	28.6	13.9	38.9	187	17	35	37	86
	MESS-1	46.1	17.8	25.5	13.3	39.4	38	38	39	35	89
	OCSS-1	15.4	3.5	20.3	3.9	19.5					
6	BCSS-1	62.7	15.4	57.3	22.3	15.2	147	14	314	29	50
	MESS-1	17.3	5.8	25.5	11.3	21.4	15	7	156	11	42
	OCSS-1	65.2	9.5	12.6	5.9	5.8					
7	BCSS-1	8.1	1.6	15.6	7.8	3.7	10	10	21	7	3
	MESS-1	11.5	4.5	3.0	5.5	12.9	11	9	3	8	13
	OCSS-1	9.6	4.6	28.7	2.9	15.3					

1. Calculated as $\frac{100}{\bar{X}}\sqrt{\frac{\sum(Xi - \bar{X})^2}{n-1}}$

2. Calculated as $\frac{100}{R}\sqrt{\frac{\sum(Xi - R)^2}{n}}$, n is used in the denominator rather than n-1 since no degrees of freedom are lost by calculating an average.

3. Only one significant figure reported, therefore roundoff error could be large. We have calculated range assuming most favourable to least favourable roundoff.

laboratories. The coefficient of variation shows the relative precision each laboratory has obtained and a wide range is evident (1% to 87%). We have summarized accuracy (which includes both a precision and bias component) by summing the squared deviations from the "reliable" value expressed as a modified coefficient of variation;

$$E\ \% = \frac{100}{R} \sqrt{\frac{\Sigma (X_i - R)^2}{n}}$$

where R is the NRC reliable value and X_i the individual determinations. The least accurate data appear in the Hg and Cd determinations, in particular the worst case being 370% for the BCSS-1 Cd determination. Laboratories 1 and 6 determined Cd by flame A.A. and it is expected that their detection limits are too high to determine Cd accurately at the ODCA concentration of 0.6 $\mu g\ g^{-1}$ (Samant et al, 1979, discuss a similar problem).

The accuracy of the laboratories, defined here as how closely determinations agreed with the NRC "reliable" value, is also summarized in Table 2. The top row for each laboratory gives the number of determinations which fall within the BCSS-1 or MESS-1 95% tolerance interval. A maximum score for each laboratory would therefore be 40, while the expected value if there were no laboratory bias but only laboratory variability is 38 (0.95 x 40). The bottom row for each laboratory shows how many of the laboratory averages (4 points) fall within the 95% tolerance limits, and is more an estimate of bias, random error being reduced by a factor of 2. Laboratory 7 performed best with 30 individual determinations and <u>all</u> averages lying within the tolerance limits. Laboratory 5 had the poorest record with only 5 determinations and one average falling within the limits. Overall performance shows that about 35% of single determinations and 40% of the averages fell within the tolerance limits. Tables 1 and 2 corroborate one another. Laboratory 7 has performed best, closely followed by laboratory 3. Laboratory 4 and laboratory 2 were about equal and could certainly improve performance for some of their metal determinations. Laboratories 1, 5 and 6 performed poorly.

The data have been subjected to the ranking procedure of Youden (1968 a) which allows one to reject data which are exceptionally high or low when all laboratories are compared. Unfortunately this democratic procedure does not

Table 2. Determinations Falling Within the NRC 95% Tolerance Limits

	LAB	Hg	Zn	Cd	Cu	Pb	Σ
1	Total (8)*	1	0	0	0	4	5
	$\bar{X}$ (2)*	0	1	0	0	1	2
2	Total	0	2	4	0	4	10
	$\bar{X}$	0	0	1	0	1	2
3	Total	5	0	7	8	0	20
	$\bar{X}$	2	0	2	2	0	6
4	Total	0	1	0	7	6	14
	$\bar{X}$	0	0	0	2	1	3
5	Total	1	1	1	2	0	5
	$\bar{X}$	0	1	0	0	0	1
6	Total	2	5	0	6	1	14
	$\bar{X}$	1	2	0	1	0	4
7	Total	4	5	6	8	7	30
	$\bar{X}$	2	2	2	2	2	10
TOTAL (56)		13	14	18	31	22	98
TOTAL $\bar{X}$ (14)		5	6	5	7	5	28

*Top row for each lab summarizes the number of determinations (maximum of 8) falling within the 95% tolerance limits given by NRC. The bottom row gives the same information for averages (maximum of 2).

guarantee that the majority are right, and this may be a particular problem when the methods used by the various laboratories are similar. Here we are able to evaluate the ranking procedure itself, since for BCSS-1 and MESS-1 we have a reliable value determined by many laboratories using several independent methods. To perform the ranking (for each metal and each sediment), the laboratories are assigned a number from 1 for the highest mean result to 7 for the lowest result. The ranks are then summed for the 12 separate determinations and compared to the approximate 5% probability limits (for seven laboratories and 12 samples the limits are 29, 67). In Table 3 the results are summarized; H for laboratories that were high and L for those that were low. This rejection process appears to be fair for BCSS-1 and MESS-1 as can be seen by examining the deviations of results from the reliable values (see Table 1). Note that in Table 3, laboratory 7 had no data which could be rejected and laboratory 3 was low only for Pb. This agrees very well with the independent check on accuracy summarized in Tables 1 and 2. Tables 4a, b show the same ranking process applied to accuracy and variance (based on the four replicates for each of the three materials). Laboratory 7 had good accuracy, while laboratory 5 had poor accuracy. Laboratories 3 and 4 had exceptionally good precision, while laboratories 6 and 5 performed poorly.

Table 3. Summary of Youden's Ranking Procedure

LAB	Hg	Zn	Cd	Cu	Pb
1	L		H		H
2	H			L	
3					L
4			L		
5		H	L	H	L
6		H	H	H	H
7					

Table 4a. Laboratory Ranking; According to Accuracy

High						Low
7	3	4	2	6	1	5

Table 4b. Laboratory Ranking; According to Variance

High Precision					Low Precision	
3	4	2	7	1	6	5

Since Youden's (1968 a) screening process and our independent accuracy assessment generally corroborated one another, we used the screening process as an aid to estimating the metal concentrations in our OCSS-1 sub-reference material. However, we found that it was not infallible; Cu determinations by laboratory 7 were accurate and precise for both BCSS-1 and MESS-1, but it is clear that their determinations for OCSS-1 are low when compared to the other laboratories. Since Cu is so high in our sediment, it is likely that extra dilution or new standards were required to determine the concentration. An error might occur here and not in the determination of BCSS-1 or MESS-1 (i.e. BCSS-1 and MESS-1 are poor choice of reference material for Cu in OCSS-1). We have used judgement in deleting these Cu determinations in Table 5. Similarly, we felt that only laboratories 3 and 7 determined Hg with sufficient precision and accuracy, and it is encouraging that they agreed very closely on the Hg contents of OCSS-1.

Table 5. Best Estimate of "Reliable Value" for our Secondary Reference OCSS-1

Metal	Laboratories Considered	$\bar{X}$	s	n	95% Conf. Interval	95% Tolerance Limit [4]
Hg	3,7	0.247	0.021	8	± 0.018	± 0.078
Zn	1,2,3,4,7 [1]	526	35	19	± 17	± 97
Cd	2,3,4,7 [2]	2.86	0.32	15	± 0.18	± 0.94
Cu	1,3,4 [3]	1,005	69	11	± 46	± 225
Pb	2,4,7	96	13	12	± 8.0	± 41

1. Rejected one low data point from laboratory 1 (Chauvenet's Criterion)

2. Rejected one high data point from laboratory 7 (Chauvenet's Criterion)

3. Laboratory 7 results rejected as too low in spite of accurate determination of lower Cu concentration in MESS-1 and BCSS-1. Rejected one low determination from laboratory 1 (Chauvenet's Criterion)

4. Two sided tolerance limit with 95% confidence that 95% of the population lies between the given limit (Natrella, 1963 p. 2-14).

4.3 Graphical Diagnosis

Youden (1968 b) has suggested a very useful procedure for examining interlaboratory test results. To apply this method, laboratories must have tested at least two different materials, and the results are diagnosed by plotting one test result versus the other. This is done for BCSS-1 and MESS-1 in Figures 1-5 for each metal. If one draws the vertical and horizontal median lines as has been done on the figures, then random errors should result in an equal distribution of data among the four quadrants. Systematic errors (laboratories which tend to get high or low results) will be diagnosed by a tendency for points to concentrate in the upper right - lower left quadrants. Data from a number of laboratories which were precise but had varying biases might be expected to approximate a line with a 45^{o} slope. Out of line points could be caused by gross errors on one or both materials.

Since the two reference sediments are similar, we assume that the dispersion of results reported for BCSS-1 is about the same as that for MESS-1. Youden (1968 b) suggests that a rough estimate of precision can be made by considering the perpendicular distance from each point to the 45^{o} line through the median intersection. For each metal we have estimated the "obtainable" precision by eliminating the poor data (the 2 or 3 worst laboratories) and calculating a standard deviation. From this standard deviation we have estimated the radius of a circle within which 99% of data points could be expected to fall if bias or systematic errors were removed, and the circle is plotted centered on the median crossing. The main advantage of figures 1-5 is that they show graphically how the laboratories are performing, and no statistical background is required to understand the results. Youden (1968 b) notes that the direction for improvement is clearly indicated. Points which lie in an elongated ellipse show procedure or calibration differences between laboratories and points far out on the 45^{o} line show very substantial procedure differences.

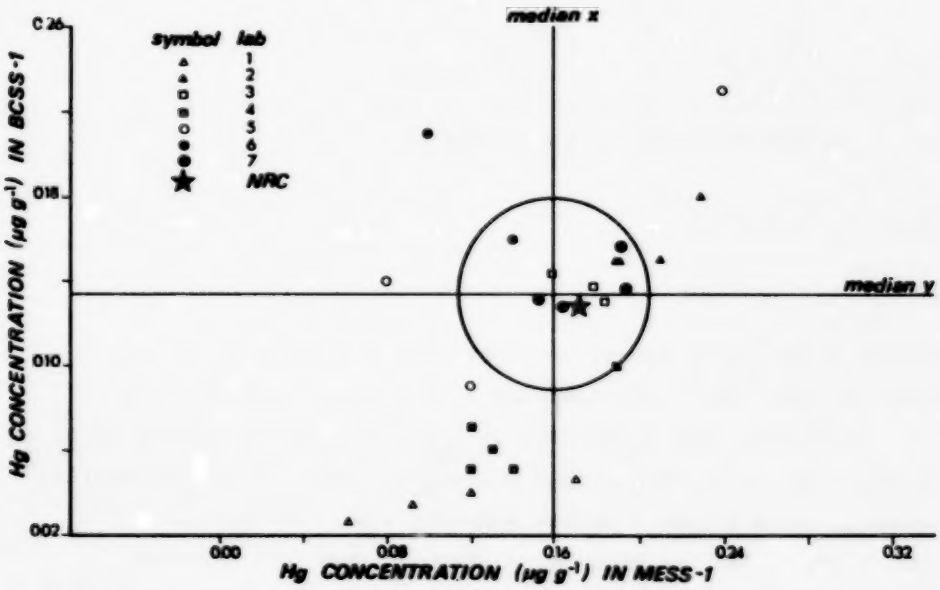


Figure 1. Youden plot for Hg

Systematic bias between laboratories is evident for Hg because points fall predominantly in the upper right-lower left quadrants. Laboratories 5 and 6 are subject to erratic determinations. Laboratories 3 and 7 are precise and accurate whereas laboratory 4 demonstrates excellent precision but the determinations appear to be slightly low. Use of reference material by laboratory 4 should assist them in providing excellent data.

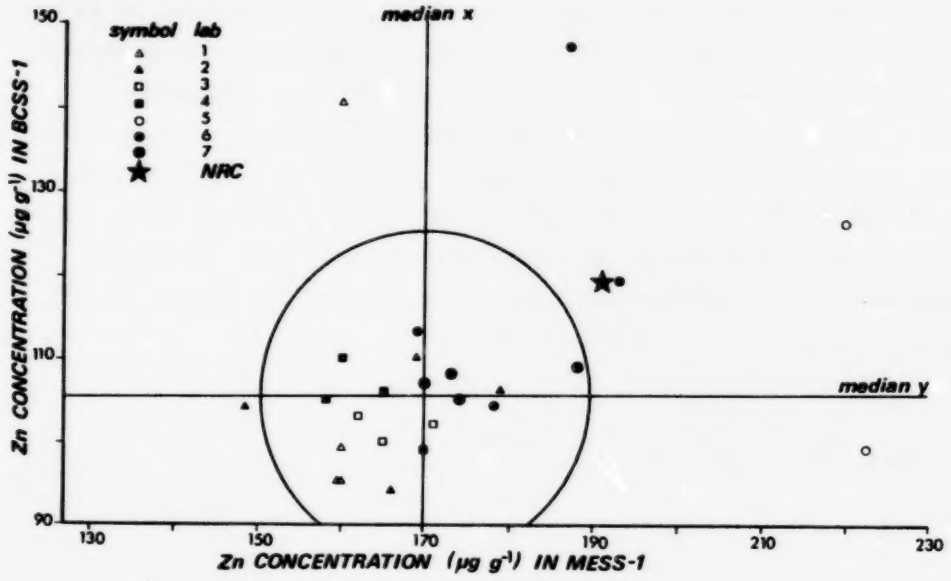


Figure 2. Youden plot for Zn

Laboratories 5 and 6 are having problems with erratic and generally high Zn determinations. With the exception of one point (laboratory 1), the other laboratories are producing data in a grouping which appears to be predominated by random error rather than systematic bias. It is interesting that this grouping falls around a median somewhat less than the Zn concentrations given by NRC for BCSS-1 and MESS-1. Over 120 separate analyses using 5 independent or quasi-independent methods in 8 facilities

were used to derive the Zn value in MESS-1 (Berman, pers. comm.) and therefore one is forced to ascribe much confidence in the NRC value. The simplest explanation for our data is that the various methods used here give incomplete Zn extraction. Berman (pers. comm.) has observed a tendency toward lower Zn results by "solution" technique (such as acid digestion/AA) as opposed to "solid" techniques (such as X-ray fluorescence spectroscopy). This point is worth keeping in mind when analyzing reference materials certified by methods different from those being used by the analyst. Indeed to emphasize the point, Cr can be under-recovered consistently by about 20% in commonly used solution techniques (Erickson, pers. comm.). All but the very careful reader might fail to see that only "solid" techniques were used to assign the MESS-1 and BCSS-1 "reliable values" for Cr.

The usefulness of reporting analyses on reference material along with the samples can be seen by looking at the Zn results from laboratory 7. They report concentrations for their own reference material (BCSS-1, MESS-1) which agree very well with the "blind" material we provided. (See Appendix 1).

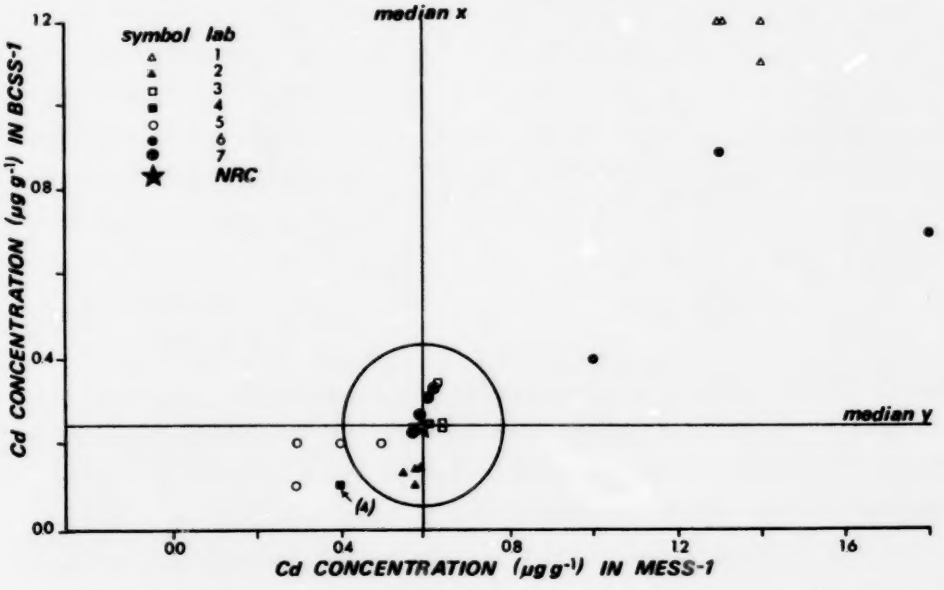


Figure 3. Youden plot for Cd

The data grouping indicates large systematic errors for Cd. Most of this can be explained by the high Cd determinations of laboratories 1 and 6, probably due to high detection limits of the flame A.A. technique or poor background correction. Laboratories 3 and 7 have performed best in terms of precision and accuracy. Laboratory 4 has excellent precision but is systematically low, while laboratory 2 has been able to measure Cd reliably at the 0.6 μg g^{-1} concentration but is low at the 0.25 μg g^{-1} level. This latter problem may be an effect of detection limit or background correction which is more important at the lower concentration.

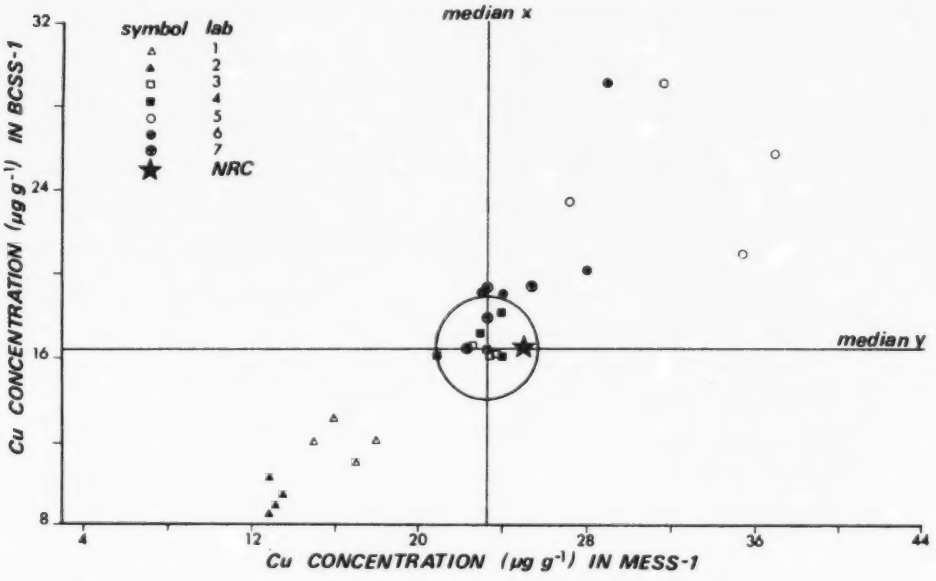


Figure 4. Youden plot for Cu

Systematic error seems to predominate in the Cu determinations but "wild" data points are not a problem. The precision which can be obtained by atomic absorption methods is very good as attested by the tightness of the circle within which 99% of the data would lie if bias were removed. Use of reference material or improvement in calibration methods should help produce data which are both precise and accurate. For laboratory 2 there may be a simple calculation error.

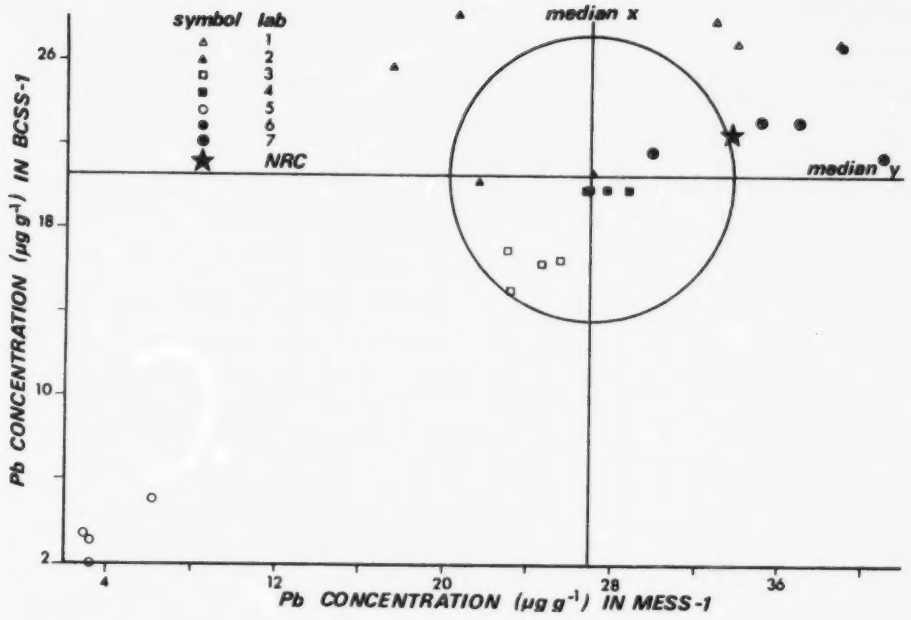


Figure 5. Youden plot for Pb

Systematic error is very important for Pb. Laboratories 3, 4 and 7 had the best precision, and laboratory 7 had the best accuracy. For laboratory 5 a problem of low recoveries is very clearly identified. Use of standards or reference materials would have revealed the poor extraction of Pb during the analysis. Laboratories 3 and 4 show that good precision is obtainable in Pb determinations.

5. CONCLUSIONS

To provide data that are accurate within known limits of confidence, laboratories must satisfy two requirements:

(1) Techniques must be applied which validate the data and allow a reasonable estimate of precision and accuracy. That is, the measurement must be in a state of control.

Table 6. Summary of Laboratory Performance and Reporting

LABORATORY	1	2	3	4	5	6	7	
								Performance
	F	G	G	G	P	P	F	Precision
	P	F	G	F	P	P	VG	Accuracy
								Reporting (See Appendix 1 for details)
	P	P	P	VP(I)	A	P	F	Precision (and method of estimating)
	P	F	G	F	-	VP	F	Precision achieved versus claimed
	A	F	A	A	A	P	F	Accuracy (and method of estimating)
	-	P	-	-	-	VP	VG	Accuracy achieved versus claimed
	F	VP	P	P	P	G	G	Laboratory methods
	P	P	G	P	P	P	P	Instrumentation
	P	A	A	P(I)	A	A	A	Calibration
	F	A	A	A	A	A	A	Recovery and interferences
	A	A	A	A	A	A	A	Blanks (and their variance)
	P	P	P(I)	P(I)	VP	P	P	Detection limit (and method of calculating)
	Yes	Yes	No	Yes	No	No	No	Numbers reported at less than detection limit
	A	A	A	A	A	A	A	Quality control measures

VG	Very good	VP	Very poor
G	Good	A	Absent
F	Fair	I	Incomplete
P	Poor		

(2) Data should be reported completely including methodology and validation. Since many statements about the data (including precision, accuracy, detection limit and blank) can be calculated in many different ways, the exact approach including equations should be shown.

That these two steps are required can be seen from the perspective of a data reviewer. Numbers which are generated by vague or unknown methods and are unaccompanied by valid error estimates are useless. Eisenhart (quoted in Taylor, 1981) states "until a measurement operation has attained a state of statistical control, it cannot be regarded in any logical sense as measuring anything at all".

Table 6 summarizes our rating of the laboratories based on the statistical tests, Youden Plots and the critique of their documentation. The rating has been split into two logical elements; the performance, which is based entirely on results, and reporting for which we consider documentation, and how well our independent estimation of precision and accuracy agrees with what the laboratory claims.

The exact categories we have chosen for the evaluation of reporting in Table 6 are arbitrary but we believe most analysts would agree on their importance to the final result. None of the laboratories have scored very well on reporting and the fault does not lie entirely with them. It is clear that individuals who require data to make decisions (in this case for ocean dumping) must specify how the data are to be reported. For example, in Table 6 no laboratories reported that they used quality control measures and while at least two laboratories in hindsight said they had such measures, it was not obvious that they had a stated quality assurance program with clear objectives.

To obtain data which are properly validated and accompanied by adequate reporting will cost more, perhaps 25% of the budget being devoted to that task alone. Initially, it is expected that the task of preparing properly written methods and setting up control systems will require considerable effort. What is urgently required is a protocol or guideline on quality control and assurance which will assist laboratories and managers alike in

achieving uniform and reliable results which will, with time, generate a useful data base. Such a data base will pay dividends in that we will be able to use it to guide sampling strategies in future surveys and to analyze time trends. At present there are few data which could be used for such ends.

In spite of the negative tone so far, we believe the results of the performance check are encouraging, particularly since none of the laboratories knew the true reasons we submitted samples for analysis. Two laboratories have provided particularly good data, and in no case are there "order of magnitude" errors. For Cd, there are problems with determination by flame A.A. (at the 0.6 $\mu g\ g^{-1}$ concentration level) and therefore flameless techniques are required for samples which contain less than about 3-5 $\mu g\ g^{-1}$. Appropriate reference materials applied correctly could also have improved the results in several cases where calculation errors, blank correction or poor extraction efficiencies appear to have caused problems.

For many environmental samples, marine sediments included, lack of agreement between replicates has often been ascribed to environmental patchiness. Variability or trends in environmental data cannot be interpreted to a greater degree of refinement than the variability from the analysis and therefore it is most important to minimize laboratory variance and also to estimate it carefully. Controls must be used to prevent sample inhomogeneity being used as an excuse for poor analytical reproducibility. With the data compiled in this report it is clear that sample inhomogeneity or poor sampling cannot be contributing significantly to the total error. In consideration of the Youden Plots the following standard deviations (Table 7) for the metals are achievable for sediments similar to BCSS-1 and MESS-1 (standard deviation may be dependent on absolute concentration of metal and matrix).

Table 7. Achievable precision for determination of Hg, Zn, Cd, Cu and Pb in reference sediments.

Metal	Metal Concentration $\mu g\ g^{-1}$	s $\mu g\ g^{-1}$	C.V. (%)
Hg	0.129- 0.171	0.015	9-12
Zn	119-191	6.5	3-6
Cd	0.25 - 0.59	0.061	10-24
Cu	18.5 - 25.1	0.73	3-4
Pb	22.7 - 34.0	5.8	17-26

Regulatory decisions should take into account the achievable precision listed above. Furthermore, it is quite reasonable to require this level of performance by any laboratory providing data for ocean dumping purposes.

Other sources of variance arise from different analysts working over a long time period within a laboratory, and between different laboratories. Youden Plots and analysis of variance indicate time and again that this variance tends to be large, and it is therefore a major problem when collecting or comparing data from many laboratories over a long time period. To address this problem requires quality control procedures which include the appropriate use of reference material. It is for this reason that we recommend that laboratories which generate data for ocean dumping evaluations must use quality control measures and fully report them along with the data.

REFERENCES

Abbey, S., 1980. Studies in "Standard Samples" for use in the general analysis of silicate rocks and minerals, Part 6: 1979 edition of "usable" values. Paper 80-14, Geological Survey of Canada, 30 pp.

AOAC, 1974. Report of the executive director. Journal of the AOAC 57 p. 449.

Harris, W.F., 1978. A critical examination of analytical error. Talanta 25, 325-329.

Ingamells, C.O., and P. Switzer, 1973. A proposed sampling constant for use in geochemical analysis, Talanta, 20, 547-568.

Kirchmer, C.J., 1983. Quality control in water analyses. Environ. Sci. Technol., 17, 174A-181A.

Ku, H.H., 1968. Expressions of imprecision, systematic error and uncertainty associated with a reported value. P. 73-78 In, Precision Measurements and Calibration; Statistical Concepts and Procedures, N.B.S. Special Publ. 300, volume 1, ed. H.H. Ku, Washington, D.C. 436 pp.

Lindgren, B.W. and G.W. McElrath, 1969. Introduction to Probability and Statistics. 3rd ed., Macmillan, Toronto, 305 pp.

Mandel, J. and T.W. Lashof, 1968. The interlaboratory evaluation of testing methods, p. 170-183. In Precision Measurement and Calibration Statistical Concepts and Procedures, N.B.S. Special Publ. 300, volume 1, ed., H.H. Ku, Washington, D.C., 436 pp.

Natrella, M.G., 1982. Selected statistical concepts useful when evaluating measurements and measurement processes. Presented at seminar on quality assurance of chemical measurements, May, 1982, unpublished manuscript.

Natrella, M.G., 1963. Characterizing the measured performance of a material, product, or process. In Experimental Statistics, p. 2-1 - 2-15, N.B.S. Handbook 91, Washington, D.C.

Natrella, M.G., and C. Eisenhart, 1968. Some basic statistical concepts and preliminary considerations. In, Precision Measurements and Calibration Statistical Concepts and Procedures, p. 277-95, N.B.S. Special Publ. 300, Volume 1, ed., H.H. Ku, Washington, D.C. 436 pp.

Samant, H.S., D.H. Loring and S. Ray, 1979. Laboratory evaluation program. First quality control round robin. Surveillance Report EPS-4-AR-79-1 Environment Canada, 38 pp.

Samant, H.S., D.H. Loring and S. Ray, 1981. Atlantic Regional laboratory quality control workshop. Surveillance Report EPS-5-AR-81-5, Environment Canada, 142 pp.

Taylor, J.K., 1981. Quality assurance of chemical measurement. Analytical Chemistry 53, 1588A - 1596A.

Thompson, M. and R.J. Howarth, 1980. The frequency distribution of analytical error. Analyst 105, 1188-1195.

Youden, W.S., 1968 a. Ranking laboratories by round robin tests. In, Precision Measurements and Calibration Statistical Concepts and Procedures, p. 165-169, N.B.S. Special Publ. 300, Volume 1, ed., H.H. Ku, Washington, D.C. 436 pp.

Youden, W.S., 1968 b. Graphical diagnosis of interlaboratory test results. In, Precision Measurements and Calibration Statistical Concepts and Procedures, p. 133-137, N.B.S. Special Publ. 300, Volume 1, ed., H.H. Ku, Washington, D.C. 436 pp.

Youden, W.S. and E.H. Steiner, 1975. Statistical manual of the association of official Analytical Chemists; Statistical techniques for collaborative tests. Association of Official Analytical Chemists, Arlington, Va, 88 pp.

Zar, J.H., 1974. Biostatistical Analysis. Prentice-Hall, Englewood Cliffs, N.J., 620 pp.

Zitko, V., 1980 a. Marine chemistry and pollution into the 80's. In, Marine Chemistry into the Eighties, p. 2-29, N.R.C.C., J.A.J. Thompson and W.D. Jamieson, eds., 202 pp.

Zitko, V., 1980 b. Sampling and analysis of sediments for the purposes of the ocean dumping control act. Problems and suggestions for solutions. In, Atlantic Region laboratory quality control workshop proceedings, p. 102-123. Samant et al eds. Surveillance Report EPS-5-AR-81-5, Environment Canada, 142 pp.

Appendix 1

DATA SUMMARIES

Samples listed in the tables were labelled as follows:

1 - Alberni - 1
2 - Howe Sound
3 - Powell River - 1
4 - Quarantine
5 - Campbell River
6 - Nanaimo
7 - Point Grey - 2
8 - Sand Heads
9 - False Creek - 1
10 - Howe Sound - 2
11 - Ladysmith
12 - Point Grey - 1

In Appendix 1, the laboratory procedures are reported verbatim except where noted.

Table A-1. Laboratory No. 1

SAMPLE	MOISTURE CONTENT % ADDED	MOISTURE CONTENT % MEASURED	SAMPLE IDENTITY	METAL CONCENTRATION (DRY WEIGHT) µg g^{-1} Hg	Zn	Cd	Cu	Pb
1	36	34	BCSS-1	0.039	95	1.2	13	35
2	-	1.5		0.025	99	1.1	11	28
3	36.4	35		0.046	140	1.2	12	27
4	43.8	42		0.034	95	1.2	12	27
			$\bar{X}$±3.18 s	0.036±0.028	107±70	1.18±0.16	12.0±2.5	29.3±12.4
			R±tol 1	0.129±0.012	119±12	0.25±0.04	18.5±2.7	22.7±3.5
5	43	44	MESS-1	0.12	160	1.3	16	36
6	26.3	26		0.062	160	1.4	17	33
7	60.1	64		0.17	160	1.4	18	39
8	-	1.4		0.092	170	1.3	15	34
			$\bar{X}$±3.18 s	0.111±0.146	163±16	1.35±0.19	16.5±4.1	35.5±8.3
			R±tol	0.171±0.014	191±17	0.59±0.10	25.1±3.8	34.0±6.1
9	45.6	47	OCSS-1 2	0.077	540	4.4	1100	140
10	49.5	50		0.15	570	3.8	1100	140
11	57.4	58		0.057	550	4.1	1100	120
12	32.2	3.4		0.085	370	2.6	800	120
			$\bar{X}$±3.18 s	0.092±0.127	508±296	3.53±2.73	1028±461	130±37

1 NRC reliable value ± 95% tolerance limit
2 OCSS-1 secondary reference prepared at IOS, Ocean Chemistry (no reliable value available).

Laboratory 1

Laboratory procedures

Heavy metals (Zn, Pb, Cd, Cu) are determined by digesting 1 g of dried and weighed soil sample in 50 mL deionized water with 10 mL of aqua-regia ($HCl:HNO_3$ = 3:1) at boiling for 2 hours in a 150 mL beaker covered with a watch glass. Add deionized water to maintain digest volume at approximately 20 mL. Filter digest (Whatman No. 42) into a 25 mL volumetric flask and make up to volume. Analyze by A.A. immediately or transfer to a polyethylene container and refrigerate. (Anderson, J., 1974, Atomic Absorption Newsletter, 13 , 31-32.) For Hg weigh out accurately 1 g or more wet sediment and transfer to 75 mL Folin tubes. Add 5 mL of combined acid (100 mL of HNO_3 plus 400 mL of H_2SO_4) and swirl to mix. (For calcareous samples add acid dropwise with swirling until CO_2 evolution subsides. For high organic content, additional acid ∿10 mL may be needed.) Place tubes in an Al heating block already at 90° C and digest approximately 1.5 hours. Cool for 15 minutes and add dropwise (carefully in fume hood) 2 mL of concentrated HCl. Heat at 90° C until brown fumes subside (∿ 1 hour), cool in a water bath and add 2 mL of 5% $K_2S_2O_8$ solution (prepared fresh daily) and let sit for 1/2 hour. Leaving tubes in cold water bath, carefully add 5 mL of 6% $KMnO_4$ with gentle swirling. Cover with parafilm and allow to stand overnight. Just before analysis, add 2 mL hydroxylamine sulphate and swirl, make up to 50 mL and analyze immediately. (Iskandar, I.K., 1972, Analyst 97, 388-393; Varian Techtron Technical Topics, Jan. 1975; Rains, T.C. and O. Mines, Analytical Chemistry Division, N.B.S.; Agemian, H. and A.S.Y. Chau, Rev. 12/69 FD-6; Water Quality Branch Methods, and In-house Manuals.)

Instrumentation

Metals (Pb, Cd, Cu, Zn) are measured with a Varian AA-6 Atomic Absorption Spectrophotometer. Mercury is measured with a Varian AA-5 Atomic Absorption Spectrophotometer (Hg hollow cathode lamp) used in the cold vapour mode with a quartz flow-through cuvette (15 cm path length).

Calibration

Add appropriate increments of 0.1 mg L^{-1} standard mercury solution to tubes for standards. A calibration curve is prepared plotting mercury vs absorbance.

Recovery and interferences

For Hg, organic mercurials will not respond to detection unless converted to mercuric ions. Potassium persulphate has been found to give 100% recovery for some organic mercurials and therefore a persulphate oxidation step can be included. Low Hg recoveries from presence of high levels of Cu, Au, Pb, Pt and $S^{=}$. $KMnO_4$ can eliminate $S^{=}$ interference (up to 20 mg L^{-1} as Na_2S in distilled water). Copper concentrations up to 10 mg L^{-1} had no effect on recovery of Hg from spiked samples. Samples high in Cl^{-} require additional $KMnO_4$ but care must be taken to remove free chlorine prior to determination. Interference can result from volatile organics, SO_2 and NO_2. A preliminary run without reagents should determine presence of this interference.

Blanks

Run 2 blanks for Cd, Pb, Zn, Cu. Blank subtracted in calculating final concentration. Run enough tubes with just reagents through digestion for 3 blanks and standards for Hg.

Detection limits (d.l.)

Minimum detectable concentration (µg g^{-1}, dry weight, based on a 1 g sample) Cd - 1.25, Cu - 1.25, Pb - 5.0, Zn - 1.25. For Hg minimum detectable level - 0.05.

Precision

Table of precision for sediment dried at 105° C and ground to pass 0.15 mm sieve. Precision presented as concentration (mg g^{-1}) ± % coefficient of variation; Cd - 0.0054 ± 5.8%, Cu - 0.0281 ± 5.8%, Pb - 0.016 ± 3.2%, Zn - 0.046 ± 4.8%.

Critique

The methodology supplied here was one of the most complete. However, there are a number of problems. During the telephone interview they implied that these laboratory instructions were not exactly the ones used, pointing out the need to update method descriptions and keep them current. The laboratory should, as was done here, date the method manual. The methods as described appear adequate and could be repeated independently. Instrumentation is not completely described because we do not know if it was flame technique or graphite furnace. From the d.l. for Cd we infer the former. For Hg, we do not know the carrier gas or its flow rate. Calibration is dealt with insufficiently since we do not know how often it is done, how many points or the zone of linearity. It is implied that 3 blanks and standards are run for Hg but we are not even sure if that is total or for each. Recovery and interferences are dealt with in the procedures guide for Hg but there seems to be no ongoing evaluation on a routine basis. That is, some spiked samples were run at one time but it is not apparent that checks are made on environmental samples. Although blanks are run, we are not told how often, the average level, or the variance on the blank. Detection limits are provided (probably to too many significant figures), but the method of calculation is not given so we really have no idea what they mean. Furthermore, four Cd concentrations are reported below the d.l.. For Hg, no precision estimates are given. The precision for the other metals is given as a coefficient of variation and, importantly, the metal level for which it is determined is also given. However, precision is reported (without describing how it was estimated) as a table in the methods manual. This is fundamentally wrong. What might be provided is a typical precision which can be obtained using the method. Precision is a fundamental property of the data as they are produced and must be determined as an integral part of the measurement process. Precision extracted from a table or a literature report is meaningless. That this is so can be seen by comparing the reported precision with that calculated from data in Table A-1. The report submitted by Laboratory 1 includes no evidence of accuracy checks, although during the phone interview we learned that NBS river sediment was used. No other quality control measures appear to have been used.

Table A-2. Laboratory No. 2

SAMPLE	MOISTURE CONTENT % ADDED	MOISTURE CONTENT % MEASURED	SAMPLE IDENTITY	METAL CONCENTRATION (DRY WEIGHT) µg g^{-1} Hg	Zn	Cd	Cu	Pb
1	38.9	38.0	BCSS-1	0.15	110	0.14	9.02	20.7
2	-	1.14		0.15	94	<0.10	10.4	20.4
3	39.1	38.1		0.18	104	0.14	8.67	20.9
4	48.1	46.4		0.15	106	0.13	7.78	17.8
			$\bar{X}$±3.18 s	0.158±0.048	104±22	<0.13±0.06	9.0±3.5	20.0±4.5
			R±tol [1]	0.129±0.012	119±12	0.25±0.04	18.5±2.7	22.7±3.5
5	45.9	44.6	MESS-1	0.21	169	0.59	13.1	27.4
6	27.8	27.4		0.19	166	0.58	12.9	21.8
7	60.8	59.2		0.23	148	0.58	12.9	28.4
8	-	1.08		0.19	179	0.55	13.5	25.9
			$\bar{X}$±3.18 s	0.205±0.060	166±41	0.58±0.06	13.1±1.0	25.9±9.2
			R±tol	0.171±0.014	191±17	0.59±0.10	25.1±3.8	34.0±6.1
9	40.6	40.4	OCSS-1 [2]	0.28	572	3.22	999	79.5
10	49.8	49.6		0.30	534	3.23	994	90.7
11	50.3	44.0		0.28	500	3.28	980	93.4
12	31.5	28.3		0.28	517	3.29	970	91.4
			$\bar{X}$±3.18 s	0.285±0.032	531±99	3.26±0.13	986±41	88.8±20.0

1 NRC reliable value ± 95% tolerance limit
2 OCSS-1 secondary reference prepared at IOS, Ocean Chemistry (no reliable value available).

Laboratory 2

Laboratory procedures

The samples are digested as received using a combination of nitric and perchloric acids. A moisture is determined gravimetrically by heating the samples at 100° C.

Instrumentation

Metals (Cd, Cu, Pb, Zn) are determined by optimized flame atomic absorption. Mercury is determined by cold vapour generation atomic absorption.

Detection limits (d.l.) ($\mu g\ g^{-1}$, given by phone)

Hg - 0.1, Zn - 0.5, Cd - 0.25, Cu - 0.5, Ph - 5.0.

Precision (given by phone)

Hg - 10%, Zn - 4-5%, Cd - 4-5%, Cu - 4-5%, Pb - 4-5%. Duplicates must be within 5%.

Accuracy

Two reference materials are run along with the samples. The respective metal concentrations for their BCSS-1, MESS-1 are listed below ($\mu g\ g^{-1}$).

		Hg	Zn	Cd	Cu	Pb
NRC	BCSS-1	0.13	112	0.27	17.0	22.3
NRC	MESS-1	0.20	183	0.65	24.0	33.5

Critique

The methods are not adequately described and could not be followed independently. Critical information such as temperature and time of digestion, and the ratio of acids is missing. Instrumentation should be described (model # and particulars). No details are given on calibration or whether interferences have been checked. No blanks were reported although

the laboratory assured us that such information could be made available. The task of evaluating these data is made very difficult by the lack of reported information. The precision estimates seem to be slightly optimistic in some cases (perhaps by a factor 2) but this may have to do with the concentrations at which they were determined and the number of replicates (neither of which is reported). The accuracy checks do not work as well as they should, which may be a result of the laboratory's approach to running reference material. During the phone interview we learned that reference material was run until they "got it right". While perhaps a good strategy for methods development, it is clearly of no use for quality control. The best example of this in Table 2 is Cu. They report almost exactly one half the certified values for BCSS and MESS. By analyzing their own certified material they should have caught what is probably a calibration or calculation error. For Cd they report numbers which are less than the "stated" detection limits (with 2 significant figures). In spite of the lack of documentation, the overall performance is not bad. It is interesting to note that their Cd concentrations are reasonable at the 0.6 $\mu g\ g^{-1}$ concentration, especially since they used a flame technique (see Samant et al, 1979). Their Hg concentrations are slightly high but they do have discriminating power and can differentiate between the two reference materials.

Table A-3. Laboratory No. 3

SAMPLE	MOISTURE CONTENT % ADDED	MOISTURE CONTENT % MEASURED	SAMPLE IDENTITY	METAL CONCENTRATION (DRY WEIGHT) µg g^{-1} Hg	Zn	Cd	Cu	Pb
1			BCSS-1	0.144	102	0.34	16.2	16.5
2				0.100	99.1	0.25	16.1	16.6
3				0.137	103	0.25	16.4	17.1
4				0.130	100	0.24	16.3	15.3
			$\bar{X}$±3.18 s	0.128±0.060	101±6	0.27±0.16	16.3±0.3	16.4±2.5
			R±tol [1]	0.129±0.012	119±12	0.25±0.04	18.5±2.7	22.7±3.5
5			MESS-1	0.159	171	0.63	23.6	24.8
6				0.190	170	0.64	23.5	25.7
7				0.178	162	0.61	22.5	23.2
8				0.183	165	0.64	23.3	23.3
			$\bar{X}$±3.18 s	0.178±0.041	167±13	0.63±0.03	23.3±1.6	24.3±3.8
			R±tol	0.171±0.014	191±17	0.59±0.10	25.1±3.8	34.0±6.1
9			OCSS-1 [2]	0.241	546	2.96	1024	79.7
10				0.227	536	2.57	996	81.4
11				0.248	545	2.70	1011	95.5
12				0.276	540	2.48	972	84.5
			$\bar{X}$±3.18 s	0.248±0.067	532±16	2.68±0.67	1011±70	85.3±22.6

1 NRC reliable value ± 95% tolerance limit
2 OCSS-1 secondary reference prepared at IOS, Ocean Chemistry (no reliable value available).

Laboratory 3

Laboratory procedures

Heavy metals (Cu, Zn, Cd, Pb) are determined in 2 g portions of oven dried sediments (105° C). Sediments are digested in nitric/perchloric acid for several hours and digests are made up to final volume with deionized water before determination. Mercury is determined on 0.2 g portions of air dried sediments. Samples are digested for 30 min at 95° C in aqua regia, then for 60 min with potassium permanganate and potassium persulphate.

Instrumentation

Heavy metals (Cu, Zn, Cd, Pb) are measured by flame atomic absorption using a Perkin-Elmer Model 5000 instrument, and background correction. The Cd concentrations when below the detection limit (8 samples) are determined by flameless A.A. (HGA 500) using the known (standard ?) additional technique. Mercury is measured by the cold vapour technique using a Pharmacia UV monitor as described in "A laboratory manual for the chemical analysis of waters, wastewaters, sediments and biological material", B.C. Water Resources Services, 2nd edition (1976).

Detection limits (d.l.) (by phone, units are $\mu g\ g^{-1}$)

Hg - 0.05, Cd - 0.5 (Flame), 0.2 (HGA), Pb - <4.

Precision (by phone)

Reported as ± 5% for all metals.

Accuracy (by phone)

Reference river sediment is analyzed periodically.

Critique

As before, lack of information is the main problem. This laboratory clearly can perform analyses which are accurate and precise, particularly for Hg and Cd. However, we could not repeat their digestion technique given the written information. They do not specify how they calibrate, whether they have checked for recovery efficiency, or how routinely they run blanks and what they are. During the phone interview they were able to supply only incomplete detection limits, and approximate precision estimates. The precision estimates seem to be slightly optimistic, but this may be due to their being determined at metal concentrations greater than some of those found in the reference material. For accuracy they run reference material but do not report values obtained or how often this is done. From Table A-3 we believe they are performing careful analyses, but without knowing the "reliable" values and having blind replicates it is impossible to judge the quality of these data.

Table A-4. Laboratory No. 4

SAMPLE	MOISTURE CONTENT % ADDED	MOISTURE CONTENT % MEASURED	SAMPLE IDENTITY	METAL CONCENTRATION (DRY WEIGHT) µg g^{-1} Hg	Zn	Cd	Cu	Pb
1				0.060	105	0.1	16	20
2				0.050	110	0.1	18	20
3				0.050	100	0.1	16	20
4				0.070	106	0.1 3	17	20 3
			BCSS-1 $\bar{X}\pm3.18$ s	0.058±0.032	105±13	0.1± 0.19	16.8±3.2	20.0± 1.9
			R±tol 1	0.129±0.012	119±12	0.25±0.04	18.5±2.7	22.7±3.5
5				0.130	158	0.4	21	28
6				0.120	160	0.4	24	27
7				0.140	170	0.4	24	29
8				0.120	165	0.4 3	23	27
			MESS-1 $\bar{X}\pm3.18$ s	0.128±0.032	163±9	0.4±0.19	23.0±4.5	27.8±3.2
			R±tol	0.171±0.014	191±17	0.59±0.10	25.1±3.8	34.0±6.1
9				0.130	540	2.5	945	110
10				0.120	560	2.6	965	115
11				0.110	525	2.5	920	108
12				0.130	535	2.6	920	108
			OCSS-1 2 $\bar{X}\pm3.18$ s	0.123±0.032	540±48	2.55±0.19	938±70	110±10

1 NRC reliable value ± 95% tolerance limit
2 OCSS-1 secondary reference prepared at IOS, Ocean Chemistry (no reliable value available).
3 Maximum "s" has been calculated assuming worst case roundoff (i.e. 0.1, 0.1, 0.1, 0.1 was 0.05, 0.05, 0.149, 0.149).

Laboratory 4

Laboratory procedures

Sediments are dried at 80° C for 12 to 24 hours. The dried sample is sieved to -80 mesh fraction through nylon and stainless steel sieves. A 1 g portion is weighed into a calibrated test tube, the sample is digested with hot 70% $HClO_4$ and concentrated HNO_3 for 2 hours. The sample volume is adjusted to 25 mL with demineralized water. Sample solutions are homogenized and allowed to settle before analyses. For Hg, the sample is digested with nitric acid plus a small amount of hydrochloric acid. Following digestion the resulting clear solution is transferred to a reaction flask connected to a closed system absorption cell. Stannous sulphate is rapidly added to reduce mercury to its elemental state. The mercury is then flushed out of the reaction vessel into the absorption cell where it is measured.

Instrumentation

For metals (Cd, Pb, Zn, Cu) a Techtron A.A.S. atomic absorption unit is used. Mercury is measured by cold vapour atomic absorption methods with a Varian spectrophotometer.

Calibration

For Hg the absorbance of samples is compared with the absorbance of freshly prepared mercury standard solutions carried through the same procedure.

Detection limits (d.l.)

Hg - 0.05 ($\mu g\ g^{-1}$, by phone), Zn - 1, Cd - 0.1, Pb - 1 (background corrected). Detection limit for Cd is 0.2 (erroneously stated as 0.1 in brochure). A value of 0.1 (½ d.l.) is used to denote a "less than" value. Elements present in concentrations below detection limits are reported as one half the detection limit, i.e. zinc - 0.5 $\mu g\ g^{-1}$.

Precision

Reported as ± detection limit.

Accuracy

Reference materials plus in-house generated sub-reference materials are analyzed routinely.

Critique

Lack of information is the main problem. For the procedures we are not sure exactly what 70% $HClO_4$ and concentrated HNO_3 means. The temperature "hot" is not specific enough. For Hg we do not know what "a small amount of HCl" is nor do we know how much $SnSO_4$ is added to the solution. Calibration could be better documented since we do not know how often it is done, or how many points are provided. No mention is made of interferences or recovery checks, or blanks. Detection limits are given but we do not know how they have been calculated. The precision reported as ± the detection limit does not indicate a true evaluation of repeatability of determinations. From Table A-4, it is evident that they maintain good precision in all cases, and do have discriminating power for all the metals. However, there does seem to be a bias in some cases (low for Hg and Cd). As with laboratory 2, their Cd determinations are reasonably good considering a flame technique is used. From the "procedures" it is not evident that they background correct for Cd. Furthermore, we are not sure what the 0.1 $\mu g\ g^{-1}$ concentration for BCSS means as it is equal to the detection limit. (It was stated by phone that determinations below the d.l. were reported as 1/2 the d.l.). Routine use of reference materials should enable them to have better accuracy.

Table A-5. Laboratory No. 5

SAMPLE	MOISTURE CONTENT % ADDED MEASURED	SAMPLE IDENTITY	METAL CONCENTRATION (DRY WEIGHT) µg g^{-1} Hg	Zn	Cd	Cu	Pb
1	:	BCSS-1	0.23±0.09[3]	146	0.2	23.2	5.0
2	:		0.60±0.39[3]	126	0.2	25.6	3.3
3	:		0.09	140	0.1	28.8	1.9
4	:		0.14	99	0.2	20.8	3.0
	:	$\bar{X}$±3.18 s	0.27±0.73	128±67	0.18±0.16	24.6±10.8	3.3±4.1
	:	R±tol 1	0.129±0.012	119±12	0.25±0.04	18.5±2.7	22.7±3.5
5	:	MESS-1	0.24±0.08[3]	317	0.5	27.3	6.2
6	:		0.15±0.06[4]	220	0.4	37.1	3.0
7	:		0.11±0.03[4]	250	0.3	31.8	3.2
8	:		0.08	223	0.3	35.7	3.2
	:	$\bar{X}$±3.18 s	0.14±0.22	243±143	0.38±0.32	33.0±1.9	3.9±4.8
	:	R±tol	0.171±0.014	191±17	0.59±0.10	25.1±3.8	34.0±6.1
9	:	OCSS-1 [2]	0.14±0.01[3]	588	2.3	1160	14.7
10	:		0.13±0.03[4]	543	2.4	1123	11.7
11	:		0.17±0.08[4]	553	2.4	1220	16.2
12	:		0.12	569	1.5	1124	10.6
	:	$\bar{X}$±3.18 s	0.14±0.06	563±64	2.1±1.3	1157±146	13.3±8.3

1 NRC reliable value ± 95% tolerance limit
2 OCSS-1 secondary reference prepared at IOS, Ocean Chemistry (no reliable value available).
3 Based on 3 replicates reported by lab ($\bar{X}$±s)
4 Based on 2 replicates " " "
5 Samples 7 and 5 (Point Grey 1, Point Grey 2) appear to have been reversed either by the reporting lab or ourselves. This has been corrected on this table.

Laboratory 5

Laboratory procedures

For metals (Zn, Cu, Pb, Cd), 2-3 g of sediment is digested in dilute nitric and perchloric acid to fuming perchloric acid. The soluble residue is taken up in water, filtered and the filtrate diluted to 100 mL. Lead and Cd were solvent extracted by adjusting 50 mL of the filtrate to pH 2.5 and diluting to 100 mL. Ten mL of 10% NH_4F, 10 mL of $NaCH_3CO_2$-HCH_3CO_2 pH 4.75 buffer, and 10 mL of 1/2% zinc diethyldithiocarbamate in methyl iso-butyl ketone is added. The mixture is agitated on a shaker for 5 min. The Pb and Cd are extracted into the MIBK (modified from Wyttenback, A and S. Bajo, 1975, Extraction with metal-dithiocarbamates as reagents, Analytical Chemistry 47 , 1813-1817). For Hg: (Walton, A., 1978, Sampling and Analysis of Marine Sediments, Ocean Dumping Report/ Section 6.12 "Cold Vapour A.A. Technique").

Instrumentation

Heavy metals (Zn, Cd, Cu, Pb) by A.A. Mercury by cold vapour A.A.

Detection limits (d.l.) (units $\mu g\ g^{-1}$, by phone)

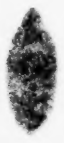
Reported as Hg - ± 0.01, Zn ± 3, Cd ± 0.1, Cu ± 3, Pb ± 0.2.

Precision (by phone).

Duplicates rarely run. Some Hg analyses were run in duplicate or triplicate. The standard deviation calculated from these is reported in Table A-5.

Accuracy (by phone).

Refer to paper (Wyttenback and Bajo, 1975) attached to report.



Critique

Lack of information is a main problem. The procedures are vague in some places and could not be independently repeated. We do not know, for example, the temperature or length of time of digestion. For mercury, the reference to Walton is sufficient for us to repeat the measurement except that two methods for Hg are described and it is not specified which one is used. Instrumentation is poorly described. There is no specification of how calibrations are performed, whether blanks are run, or whether they check for recovery efficiency. This latter oversight probably results in their very poor Pb determinations. Their detection limits, reported as plus or minus, show that they do not know exactly what a detection limit is. No estimates of precision were available. As noted with Laboratory 1, one cannot determine analytical accuracy by referring to a literature value. Analytical accuracy, and precision are intrinsic properties of each data set and dependent on the analytical vagaries belonging to that set. There is no evidence that any quality control measures are used by the laboratory.

Table A-6. Laboratory No. 6

SAMPLE	MOISTURE CONTENT % ADDED	MOISTURE CONTENT % MEASURED	SAMPLE IDENTITY	METAL CONCENTRATION (DRY WEIGHT) µg g^{-1} Hg	Zn	Cd	Cu	Pb
1	38.9	38.5	BCSS-1	0.31	104	0.70	19	35
2	-	0.93		0.46	147	0.89	29	27
3	37.3	43.8		0.16	113	0.40	19	32
4	43.8	41.3		0.10	119	1.60	20	39
			$\bar{X}$±3.18 s	0.26±0.51	121±60	0.90±0.51	21.8±15.6	33.3±16.2
			R±tol 1	0.129±0.012	119±12	0.25±0.04	18.5±2.7	22.7±3.5
5	46.2	45.8	MESS-1	0.16	178	1.8	24	42
6	30.7	28.7		0.17	187	1.3	29	39
7	60.5	54.5		0.14	169	1.0	23	41
8	-	1.10		0.21	193	1.7	28	60
			$\bar{X}$±3.18 s	0.17±0.10	182±35	1.45±1.18	26.0±9.2	45.5±30.8
			R±tol	0.171±0.014	191±17	0.59±0.10	25.1±3.8	34.0±6.1
9	38.0	39.2	OCSS-1 2	0.18	680	6.0	1066	132
10	49.4	50.6		0.10	767	5.2	1206	146
11	50.0	51.1		0.06	670	5.2	1082	129
12	36.8	36.8		0.04	610	4.4	1078	131
			$\bar{X}$±3.18 s	0.10±0.19	682±207	5.2±2.1	1108±210	134±25

1 NRC reliable value ± 95% tolerance limit
2 OCSS-1 secondary reference prepared at IOS, Ocean Chemistry (no reliable value available).

Laboratory 6

Laboratory procedures

Samples were prepared in according with Environment Canada - Department of Fisheries and Oceans Laboratory Manual Standard procedures. [For Zn, Pb, Cd and Cu, sample is freeze dried and sieved (100 mesh stainless steel). Approximately 0.5 g of sediment is digested in 5 mL deionized water, 4.5 mL of HCl and 1.5 mL HNO_3 (aqua regia) on a low heat for 3 hours. If sample froths or bumps violently, the heat is too high. The sample is then cooled and diluted to 50 mL, shaken and allowed to sit overnight. For Hg, 0.5 ± 0.1 g of sediment is digested with 8.0 mL of 1:2 HNO_3:H_2SO_4, and swirled. Then 1.0 mL of HCl is added with swirling. The solution is then boiled until vapour changes from reddish-brown to white. The 100 mL beaker is removed, cooled to room temperature and 4 mL of 3% w/v $K_2S_2O_8$ is added. After leaving overnight, solution is filtered (GF/A filter) into a reaction tube and diluted to 60.0 mL with deionized water. Mercury is then determined by a cold vapour technique. Argon flow is set to 40 mL min^{-1} and switched to dispersion tube. The reaction tube is placed on the apparatus and 6.0 mL of 1% w/v hydrazine sulfate, 3% w/v stannous chloride are injected. Mercury is determined at 253.7 nm and background absorbance is measured at 254.7 nm using a tin hollow cathode lamp. - method précis by authors].

Instrumentation

Zn, Cd, Cu and Pb were determined by atomic absorption spectroscopy, Hg by cold vapour atomic absorption spectroscopy.

Detection limits (d.l.) (μg g^{-1}, by phone)

Hg - 0.01, Zn - 0.15, Cd - 0.1, Cu - 0.1, Pb - 1.0. These values were calculated as 2 times background noise.

Precision (by phone)

Hg - 2.4%, Zn - ∿1.4%, Cd - 1.4%, Cu - ∿1.4%, Pb - 1.4%.

Accuracy (by phone)

Hg - ± 2%, Zn - ∿ ± 4%, Cd - ± 4%, Cu∿ ± 4%, Pb - ± 4%

Critique

We found the methods to be adequately described in the manual. The description of instrumentation is vague (no model numbers). There were no details on calibration, recovery and interference or blanks, although interferences were discussed in the reference. The detection limits were calculated as 2x the background noise which may reflect instrumental detection but probably not overall detection. The precision estimates are very optimistic, as shown in Table A-6 and we have no idea how they were calculated. We are not sure what they mean by accuracy due to insufficient detail in reporting, but their estimates are much too low. Note particularly Cd and Hg, the elements of major ocean dumping interest. There is no indication that quality control measures are used by this laboratory.

Table A-7. Laboratory No. 7

SAMPLE	MOISTURE CONTENT % ADDED MEASURED	SAMPLE IDENTITY	METAL CONCENTRATION (DRY WEIGHT) µg g^{-1}				
			Hg	Zn	Cd	Cu	Pb
1		BCSS-1	0.137	105	0.23	17.8	21.9
2			0.129	107	0.22	19.2	23.2
3			0.154	109	0.33	19.3	23.3
4			0.132	108	0.31	16.3	21.7
		$\bar{X}$±3.18 s	0.138±0.035	107±6	0.29±0.13	18.2±4.5	22.5±2.5
		R±tol 1	0.129±0.012	119±12	0.25±0.04	18.5±2.7	22.7±3.5
5		MESS-1	0.194	174	0.58	23.3	30.1
6			0.164	170	0.59	23.1	37.1
7			0.191	188	0.62	25.4	35.3
8			0.153	173	0.61	22.4	41.3
		$\bar{X}$±3.18 s	0.176±0.064	176±25	0.60±0.06	23.6±4.1	36.0±14.6
		R±tol	0.171±0.014	191±17	0.59±0.10	25.1±3.8	34.0±6.1
9		OCSS-1 2	0.270	466	3.06	752	72.6
10			0.260	451	4.98	755	105
11			0.225	502	3.16	759	86.1
12			0.225	464	2.78	712	94.1
		$\bar{X}$±3.18 s	0.245±0.073	470±70	3.50±3.18	745±70	89.5±43.2

1 NRC reliable value ± 95% tolerance limit
2 OCSS-1 secondary reference prepared at IOS, Ocean Chemistry (no reliable value available).

Laboratory 7

Laboratory procedures

Samples are dried at 70° C for 48 hours (Cu, Cd, Zn, Pb) then crushed to a fine powder in an agate mortar. Approximately 0.5 g is transferred to a Teflon bomb to which is added 2 mL of aqua regia and 12 mL HF. The bomb is sealed and heated at 100° C for 1 hour. After cooling, the contents are transferred quantitatively to a 30 mL polyethylene bottle containing 2.0 g of boric acid and the solution is made to a total weight of 30.0 g with Milli-Q water. Total mercury is determined on dried, crushed sediment by the procedure of Agemian and Chau (Analyst, 1976 101 , 91).

Instrumentation

For Cu, Cd, Pb and Zn flame or flameless A.A. was used depending on levels.

Blanks

These were treated the same as samples.

Detection limits (d.l.) ($\mu g\ g^{-1}$)

Hg - 0.005 (depending on reagent), Zn - 0.3, Cd - 0.001 (HGA), Cu - 5, Pb - 1.8. Calculated as twice background (noise).

Precision

Hg - 5.8%, Zn - 2.6%, Cd - 4.9%, Cu - 3.0%, Pb - 3.0%. Samples and references were analyzed in duplicate. The percent relative deviation averaged for each element gives the overall relative error between duplicate samples (sic).

Accuracy

Two reference sediments were run along with our sample. The laboratory reported the following concentrations ($\mu g\ g^{-1}$) for their reference material;

	Hg	Zn	Cd	Cu	Pb
BCSS-1	0.125 ± 0.015	107 ± 1	0.27 ± 0.02	17.8 ± 0.1	20.3 ± 1.6
MESS-1	0.173 ± 0.020	183 ± 8	0.63 ± 0.04	25.3 ± 0.5	30.0 ± 2.8

Critique

Laboratory procedures could be followed, but the description of instrumentation is weak. The laboratory notes that blanks were run but supplies no details on frequency, variance and level. The detection limits are probably instrumental and therefore do not strictly apply to the whole procedure. The precision estimate could probably be improved and clarified since we do not know what formula was employed nor how many replicates were used. Their duplicates seem to give optimistic precision perhaps because they are run closely spaced in time resulting in better agreement than might be expected on a day-to-day basis. It should be noted that their standard deviation for both reference materials agrees very well with that found in Table A-7 for all metals. This laboratory routinely runs reference material but it is not known what other quality control procedures are used. Table A-7 leads us to believe that their analytical procedures are producing reliable data.

APPENDIX 2

Data sheets for the reference sediments used in this study.

Marine Sediment Reference Materials MESS-1, BCSS-1

In tables 1-7 of the text, reliable values for the reference materials are reported. These have been extracted from the N.R.C. circular shipped with the reference materials. The following pertinent information is contained in the circular.

Reliable values are based on results of determinations by at least two independent methods of analysis. The uncertainties represent 95% tolerance limits for an individual sub-sample. That is 95% of samples, 500 mg or greater, from any bottle would be expected to have concentrations within the specified range 95% of the time.

Trace Elements - $\mu g\ g^{-1}$

	MESS-1	BCSS-1
Hg(cm)	0.171 ± 0.014	0.129 ± 0.012
Zn (fimnx)	191 ± 17	119 ± 12
Cd(gm)	0.59 ± 0.10	0.25 ± 0.04
Cu(fgim)	25.1 ± 3.8	18.5 ± 2.7
Pb(fgimpx)	34.0 ± 6.1	22.7 ± 3.4

c - cold vapour atomic absorption spectrometry
f - flame atomic absorption spectrometry
g - graphite furnace atomic absorption spectrometry
i - inductively coupled plasma - atomic emission spectrometry
m - isotope dilution solid source mass spectrometry
n - instrumental neutron activation analysis
p - instrumental photonuclear activation analysis
x - x-ray fluorescent spectrometry

These reference materials are primarily intended for use in the calibration of procedures and the development of methods used for the analysis of marine sediments and materials with similar matrices.

They were obtained by MacLaren Plansearch Ltd., Dartmouth, N.S., from the Gulf of St. Lawrence (MESS-1 from the Miramichi River estuary and BCSS-1 from the Baie des Chaleurs). They were freeze-dried (Freeze-Dry Foods, Oakville, Ont.), screened to pass a No. 120 (125 μm) screen, blended and bottled by Chemistry Division staff using the facilities of the Canada Centre for Mineral and Energy Technology in Ottawa. After bottling the samples were radiation sterilized by Atomic Energy of Canada, Ltd., to minimize effects from biological activity.

Although initially free from moisture following the freeze drying, the materials, which contain sea salt, have picked up moisture during subsequent operations. They should be dried to a constant weight before use. Drying for several hours at 105°C has proven to be a relatively simple method to achieve a dry weight for most purposes. They should be kept well sealed and in a cool place.

Randomly selected bottles were used for the analytical determinations. Results from different bottles showed no significant differences compared to results from sub-samples within bottles. Nor was there any correlation between values obtained and bottle sequence. Thus, it is assumed that all bottles of each of these materials have essentially the same composition.

National Research Council of Canada
Division of Chemistry
Marine Analytical Chemistry
Standards Program
(Dr. Shier Berman)
January, 1981

POOR

QUALITY

ORIGINAL